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Cu(I) Complexes with Heterocyclic Thiones and Triphenylphosphine as Ligands. The Crystal Structure of [Cu(tzdtH)$_2$(PPh$_3$)$_2$]NO$_3$

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Abstract

The reactions of bis(triphenylphosphine)copper(I) nitrate with heterocyclic thiones (L) [L = pyridine-2-thione (py2SH), pyridine-4-thione (py4SH), pyrimidine-2-thione (pymtH), 1,3-thiazolidine-2-thione (tzdtH), 1-methyl-1,3-imidazoline-2-thione (meimtH), benz-1,3-imidazoline-2-thione (bzimtH$_2$), benz-1,3-thiazoline-2-thione (bztzH), benz-1,3-oxazoline-2-thione (bzoxtH), 5-nitro-2-benz-1,3-imidazoline-2-thione (nbzimtH$_2$) and quinazolinone-2-thione (qnotH$_2$)] lead to the formation of mononuclear complexes of the general formula [Cu(L)$_2$(PPh$_3$)$_2$]NO$_3$. The complexes have been characterized by elemental analysis, infrared, UV–Vis and NMR spectroscopy. The crystal structure of [Cu(tzdtH)$_2$(PPh$_3$)$_2$]NO$_3$ has been determined by single-crystal X-ray diffraction methods. The colorless crystals are monoclinic, space group $P2_1/c$ with $a = 16.314(2)$, $b = 9.981(2)$, $c = 25.799(3)$ Å, $\beta = 89.39(1)°$, $V = 4200$ Å^3 and $Z = 4$.

Introduction

The coordination compounds of copper(I) with heterocyclic thione donors as ligands have been of considerable interest recently because of their stereochemistry [1, 2] and their wide ranging applications in industry and in many areas of medical–biological systems [3, 4]. Previous papers [5–8] dealt with the preparation, properties and structure of coordination compounds of copper(I) with several thiones. Mononuclear and dinuclear complexes with trigonal or tetrahedral copper(I) together with a combination of terminal and/or bridging (μ_2) S-donating ligands have been studied extensively [9–11].

A problem relating to the binding of heterocyclic thione donors to Cu(I) is concerned with coordination in the presence of nucleophilic reagents e.g. triphenylphosphine (PPh$_3$). Recently, dinuclear complexes [Cu(L)(PPh$_3$)X]$_2$ (X = Cl, Br, I; L = thione) were isolated by reaction of [Cu(PPh$_3$)X]$_4$ with pyridine-2-thione (py2SH), pyridine-4-thione (py4SH), pyrimidine-2-thione (pymtH) [12]. On the other hand, the mononuclear mixed-ligand complex Cu(py2SH)(PPh$_3$)$_2$Br can be obtained via the reaction of Cu(PPh$_3$)$_3$Br with Zr(py2SH)$_4$ in THF [12]. However, a simple method for the preparation of such complexes of general formula Cu(L)(PPh$_3$)$_2$X is the direct reaction of Cu(I) halides with the above thiones in the presence of triphenylphosphine.

As part of a more extensive study of the mixed-ligand complexes of Cu(I), we report in this paper the preparation and characterization of a series mononuclear cationic Cu(I) complexes of the general formula [Cu(L)$_2$(PPh$_3$)$_2$]NO$_3$.

Experimental

Physical Measurements

Elemental analyses were performed on a Perkin-Elmer 240 B Elemental Analyzer. NMR spectra were recorded on a Bruker AW 80 spectrometer. Infrared spectra were recorded in the 4000–250 cm^{-1} region on a Perkin-Elmer 467 spectrophotometer using KBr pellets. Electronic spectra in chloroform solutions were obtained on a Cary 17 DX spectrophotometer. Conductivity measurements were done in a Wheatstone bridge Model RC 216 B2 using 10^{-3} M solutions in acetonitrile. Melting points were determined with a Büchi apparatus and are uncorrected. Magnetic susceptibility measurements were taken employing the Faraday technique at different magnetic field strengths. Hg[Co(SCN)]$_4$ was used as the calibrant.

Starting Materials

All thione ligands, supplied by EGA or Aldrich, were purified by recrystallization from ethanol. Hydrated copper(II) nitrate, triphenylphosphine and

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all solvents were of reagent grade and were used without further purification in synthetic work. Bis-(triphenylphosphine)copper(I)nitrate was prepared according to the method of Cotton and Goodgame [13].

Preparation of the Complexes

$Cu(PPh_3)_2NO_3$ was suspended in ethanol or acetone and treated with a 1:2 mole ratio of the appropriate ligand dissolved in the same solvent. The reaction mixture was stirred for 1 h at 40 °C, filtered, and cooled to room temperature. Slow evaporation of the solvent at room temperature gave a microcrystalline solid, which was filtered off, washed with ethanol and ether and dried in vacuum. The yield in this procedure was about 70%.

Collection and Reduction of Intensity Data

Single crystals of $[Cu(tzdtH)_2(PPh_3)_2]NO_3$ suitable for the subsequent crystal structure analysis were obtained by slow evaporation of a THF solution of $[Cu(tzdtH)_2(PPh_3)_2]NO_3$.

Complete crystal and intensity collection data are reported in Table 1. Preliminary oscillation and Weissenberg photographs indicated the space group $P2_1/c$. Unit cell dimensions were derived from least-squares refinement of the setting angles of 15 automatically centered reflections in the range $51° < 2\theta < 54°$ on a Syntex $P2_1$ diffractometer. The intensities of three standards monitored after every 67 reflections were stable, with a scatter of less than 3% from their respective means. Lorentz, polarization and numerical absorption correction were applied and the data were reduced using the SHELX 76 program [14].

TABLE 1. Summary of Crystal and Intensity Collection Data

Formula	$CuP_2S_4C_{42}N_2H_{40}\cdot NO_3$
M_r	920.9
a (Å)	16.314(2)
b (Å)	9.981(2)
c (Å)	25.799(3)
β (°)	89.39(1)
V (Å^3)	4200(1)
Z	4
D_{calc} (Mg m^{-3})	1.456
D_{meas} (Mg m^{-3})	1.44
Space group	$P2_1/c$
Crystal dimensions (mm)	0.4 × 0.17 × 0.4
Radiation	Cu K$\bar{\alpha}$ (λ = 1.54178)
μ (cm^{-1})	35.25
Transmission factors	0.7642–0.5061
Scan speed (°/min)	2.0–17.0
Scan range (°)	1.7 plus $\alpha_1-\alpha_2$
Background counting (s)	0.5 of scan time
2θ limit (°)	115.0
Data collected/unique/R_{int}	6662/5735/0.0112
Data used	4870 with $F_o \geqslant 6.0\,\sigma(F_o)$
Data form h, k, l	$-17 \rightarrow 17, 0 \rightarrow 10, 0 \rightarrow 28$
Weighting scheme	$1/w = \sigma^2(F_o) + 0.0001\,F_o^2$
$F(000)$	1840
No. refined parameters	436
$\lvert\Delta\sigma\rvert_{max}$	0.268
$(\Delta p)_{max}//(\Delta p)_{min}$ (e Å^{-3})	0.773//−0.803
S^a	6.51
R^b (obs./all data)	0.0411/0.0506
$R_w{}^c$ (obs./all data)	0.0510/0.0554

$^aS = [\Sigma w(\Delta F)^2/(N-P)]^{1/2}$, P = no. of parameters, N = no. of observed reflections. $^bR = \Sigma|\Delta F|/\Sigma|F_o|$. $^cR_w = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$.

Solution and Refinement of the Structure

The positional coordinates of Cu, S1, S3 and the P atoms were deduced by the direct methods using the SHELX 86 program [15]. The rest of the non-H atoms were revealed by subsequent ΔF calculations. The phenyl rings were refined as regular hexagons with bond lengths equal to 1.385 Å. Refinement was carried out by blocked full matrix least-squares, in which $\Sigma w\Delta^2$ was minimized. The weight for each reflection was initially unity and in the final cycles given by $1/w = \sigma^2(F_o) + 0.0001\,F_o^2$, chosen so that the average values of $w\Delta^2$ for ranges of increasing F_o were almost constant. All the H atoms were calculated as riding on carbon or nitrogen atoms at 1.00 Å distance except H1 that was free. Non-H- atoms were refined using anisotropic and H atoms isotropic temperature factors. Atomic scattering factors were taken from International Tables for X-ray Crystallography [16].

Results and Discussion

Reaction of $Cu(PPh_3)_2NO_3$ with the ligands investigated, afforded microcrystalline complexes of the general formula $[Cu(L)_2(PPh_3)_2]NO_3$ which were found to be quite stable in the atmosphere. Table 2 lists the compounds with their colours, melting points, conductivities and analytical data. The results of the elemental analyses for the complexes show good agreement with the suggested formulae. The complexes are insoluble in water but are slightly soluble in common organic solvents such as chloroform, benzene, ethanol, acetone and acetonitrile.

All the isolated complexes are diamagnetic, as would be expected for d^{10} species. Their conductivity measurements in acetonitrile are in agreement with that expected [17, 18] for 1:1 electrolytes, but their chloroform or acetone solutions show a non-electrolytic nature.

Description of the Structure

The fractional atomic coordinates of the non-H atoms are listed in Table 3. Table 4 lists selected bond lengths and angles. See also 'Supplementary Material'. An ORTEP [19] diagram of the molecule is given in Fig. 1 and a stereoview [19] of the molecular packing in Fig. 2.

TABLE 2. Some Physical Properties and Analytical Data of the Complexes

Compound		Yield (%)	Color	Melting point (°C)	Λ_m[a]	C(%)[b]	N(%)	H(%)	Cu(%)
I	$[Cu(py2SH)_2(PPh_3)_2]NO_3$	68	yellow	132	148.9	62.93(63.32)	4.68(4.81)	4.52(4.62)	7.45(7.28)
II	$[Cu(py4SH)_2(PPh_3)_2]NO_3$	65	orange	102–103	120.3	62.88(63.32)	5.09(4.81)	4.55(4.62)	7.34(7.28)
III	$[Cu(pymtH)_2(PPh_3)_2]NO_3$	75	yellow	154–155	144.7	60.74(60.43)	7.83(8.00)	4.41(4.38)	7.34(7.26)
IV	$[Cu(tzdtH)_2(PPh_3)_2]NO_3$	58	colourles	182 d[c]	133.0	61.36(61.19)	4.88(5.09)	4.87(4.89)	8.00(7.70)
V	$[Cu(meimtH)_2(PPh_3)_2]NO_3$	69	colourles	129	146.7	60.14(59.88)	7.76(7.93)	5.04(5.25)	7.43(7.20)
VI	$[Cu(bzoxtH)_2(PPh_3)_2]NO_3$	64	pale yellow	136	151.8	63.12(63.05)	4.19(4.41)	4.46(4.23)	6.80(6.67)
VII	$[Cu(bztzH)_2(PPh_3)_2]NO_3$	70	pale yellow	145	139.3	61.14(60.99)	4.40(4.26)	4.29(4.10)	6.60(6.45)
VIII	$[Cu(bzimtH_2)_2(PPh_3)_2]NO_3$	69	colourles	184	157.5	63.03(63.14)	7.28(7.36)	4.54(4.45)	6.81(6.68)
IX	$[Cu(qnotH_2)_2(PPh_3)_2]NO_3$	65	pale yellow	174	155.9	62.38(62.05)	6.61(6.95)	4.37(4.20)	6.40(6.31)
X	$[Cu(nbzimtH_2)_2(PPh_3)_2]NO_3$	69	yellow	154	152.5	57.16(57.71)	9.10(9.42)	3.97(3.87)	6.30(6.10)

[a] Molar conductance values (ohm^{-1} cm^2 mol^{-1}) on freshly prepared 10^{-3} M solutions in acetonitrile. [b] Calculated values in parentheses. [c] d = decomposition.

TABLE 3. Positional and Equivalent Thermal Parameters ($\times 10^4$) of Non-H Atoms

Atom	x	y	z	U[a]
Cu	2678.9(3)	1221.7(5)	3689.6(2)	392
P(1)	2650.7(5)	830.7(8)	2814.5(3)	360
P(2)	1589.1(5)	758.7(9)	4240.1(3)	383
S(1)	3820.4(5)	−28(1)	3991.5(3)	487
S(2)	4091.5(7)	2021(1)	4826.0(4)	653
S(3)	2792.6(7)	3591(1)	3773.8(4)	647
S(4)	4567.5(9)	3322(2)	3459.6(6)	1130
C(1)	3908(2)	398(4)	4626(1)	422
C(2)	3915(2)	86(4)	5535(1)	554
C(3)	4171(2)	1547(4)	5497(2)	604
C(4)	3791(3)	4020(4)	3822(1)	615
C(5)	5335(3)	4264(6)	3766(2)	1034
C(6)	4943(4)	5198(6)	4141(2)	1107
N	6762(3)	3631(5)	4728(2)	901
N(1)	3862(2)	−421(4)	5012(1)	508
N(2)	4082(2)	4942(4)	4141(1)	816
O(1)	6377(2)	3161(3)	5102(1)	873
O(2)	7057(3)	2864(5)	4406(2)	1338
O(3)	6831(4)	4836(5)	4707(2)	1789

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$. See also 'Supplementary Material'.

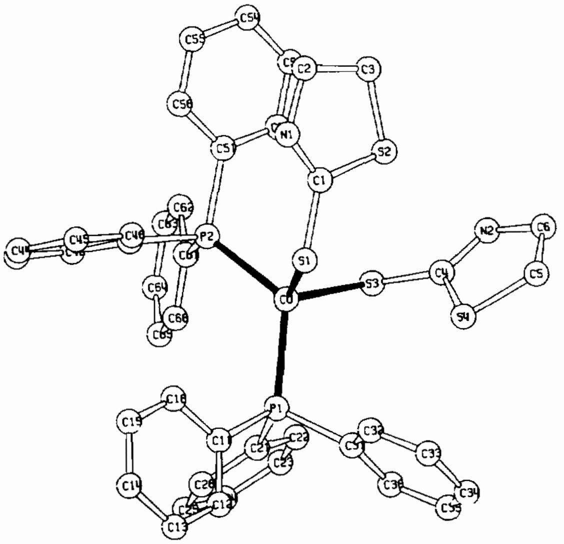

Fig. 1. A view of the complex with atom labels.

The crystals contain discrete monomeric $[Cu(tzdtH)_2(PPh_3)_2]NO_3$ units bridged by N–H···O hydrogen bonds. Each copper atom is surrounded by two sulphur and two phosphorus atoms in a distorted tetrahedral coordination. The Cu–S bond lengths are comparable with the sum (2.39 Å) of the corresponding tetrahedral radii [20]. Both Cu–S distances (Cu–S(1) = 2.373 and Cu–S(3) = 2.382 Å) are longer than the distances of 2.339 and 2.360 Å found in tetrakis(imidazolidine-2-thionato)copper(I)nitrate and (dichloro-μ-imidazolidine-2-thionato)dicopper(I) com-

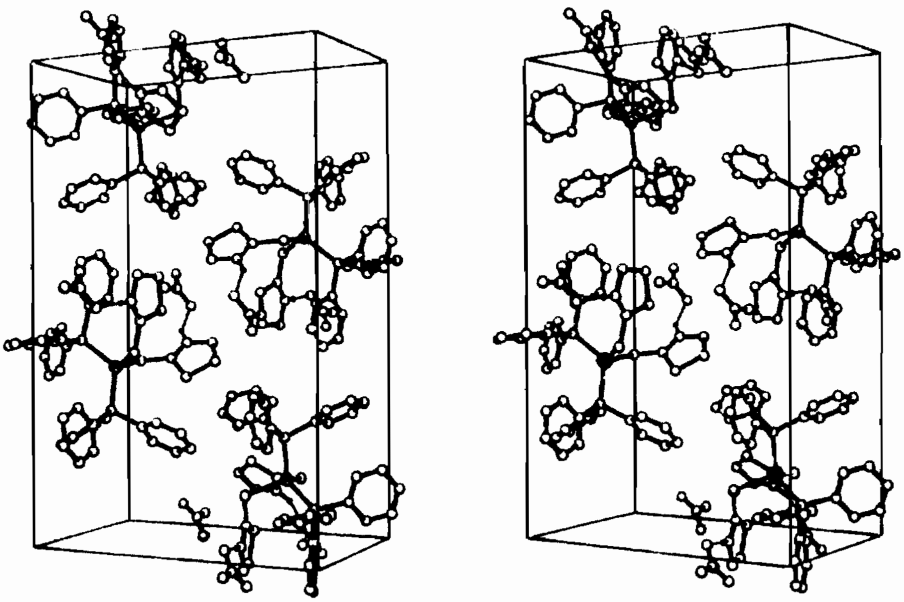

Fig. 2. A stereoview of molecular packing. Thin lines denote N–H···O hydrogen bonds.

TABLE 4. Selected Interatomic Distances (Å) and Angles (°)[a]

Cu–P1	2.292(1)	C1–S2	1.727(4)
Cu–P2	2.310(1)	S2–C3	1.800(4)
Cu–S1	2.373(1)	C3–C2	1.520(6)
Cu–S3	2.382(1)	C2–N1	1.444(5)
P1–C11	1.834(2)	N1–C1	1.291(5)
P1–C21	1.840(2)	S3–C4	1.690(4)
P1–C31	1.844(2)	C4–S4	1.714(4)
P2–C41	1.842(2)	S4–C5	1.760(6)
P2–C51	1.846(2)	C5–C6	1.484(8)
P2–C61	1.850(2)	C6–N2	1.427(7)
S1–C1	1.698(3)	N2–C4	1.326(5)
P1–Cu–P2	123.2(0)	P1–C31–C32	115.6(2)
P1–Cu–S1	104.9(0)	P1–C31–C36	124.4(2)
P2–Cu–S1	107.1(0)	P2–C41–C42	122.9(2)
P1–Cu–S3	105.1(0)	P2–C41–C46	117.1(1)
P2–Cu–S3	101.7(0)	P2–C51–C52	118.0(2)
S1–Cu–S3	115.4(0)	P2–C51–C56	121.8(2)
Cu–P1–C11	118.8(1)	P2–C61–C62	122.2(1)
Cu–P1–C21	112.6(1)	P2–C61–C66	117.8(2)
Cu–P1–C31	112.7(1)	S1–C1–S2	122.7(2)
Cu–P2–C41	113.3(1)	S1–C1–N1	125.5(3)
Cu–P2–C51	116.4(1)	S2–C1–N1	111.8(3)
Cu–P2–C61	115.2(1)	C1–N1–C2	119.8(3)
C11–P1–C21	104.2(1)	N1–C2–C3	107.2(3)
C11–P1–C31	101.4(1)	C2–C3–S2	106.9(3)
C21–P1–C31	105.6(1)	C3–S2–C1	93.2(2)
C41–P2–C51	103.0(1)	S3–C4–S4	124.4(3)
C41–P2–C61	104.3(1)	S3–C4–N2	125.0(3)
C51–P2–C61	103.0(1)	C4–N2–C6	118.8(4)
P1–C11–C12	121.6(2)	N2–C6–C5	107.8(4)
P1–C11–C16	118.4(2)	C6–C5–S4	108.9(4)
P1–C21–C22	118.1(2)	C5–S4–C4	93.6(2)
P1–C21–C26	121.7(2)	S4–C4–N2	110.7(3)

[a] e.s.d.s given in parentheses.

plexes [6]. The Cu–P(1) and Cu–P(2) distances of 2.292 and 2.310 Å, respectively, are significantly longer than those found in bis(triphenylphosphine)-copper(I)nitrate by Messmer and Palenik [21]. Three of the angles around Cu are nearly those of a regular tetrahedron while the P–Cu–P angle (123.2°) deviates considerably from the tetrahedral value of 109.47°. Lippard and Melmed [22] found a P–Cu–P′ angle of 123.26° in borohydridobis(triphenylphosphine)copper(I) and suggest that the distortion may be due to steric effects. The six independent phosphorus–carbon bond lengths are in good agreement with those found in other copper(I)triphenylphosphine complexes [23–26].

One of the tzdtH ligands (C4, S4, C5, C6, N2) is disordered (we were not able to resolve the disorder) and its atoms have large temperature factors (Table 3) and the bond distances and angles cannot be reliable. The other tzdH ligand is ordered and its bond distances and angles are in good agreement with those in other tzdtH complexes [27–28]. The exocyclic C–S bond lengths (1.698 and 1.690 Å) are typical for exocyclic thiones [29]. Our complex seems to be the first compound to be structurally characterized in the class $[Cu(thione)_2(PPh_3)_2]^+$.

Figure 2 shows a view of the crystal packing. The isolated $[Cu(tzdtH)_2(PPh_3)_2]^+$ ions are connected to the planar nitrate ions through hydrogen bonds N–H···O,

$$\left[\begin{array}{l} \text{N1–H1}\cdots\text{O1}\ (-x, -y, -z);\ \text{N1}\cdots\text{O1} = 2.779\ \text{Å},\\ \hfill \text{N1–H1}\cdots\text{O1} = 176^\circ \\ \text{N2–H2}\cdots\text{O2}\ (-x, 1-y, -z);\ \text{N2}\cdots\text{O2} = 2.815\ \text{Å},\\ \hfill \text{N2–H2}\cdots\text{O2} = 146^\circ \end{array}\right]$$

the presence of which is shown also from IR spectra.

TABLE 5. Selected Spectroscopic Data (cm^{-1})

Compound	ν(NH)	Thioamide II	Thioamide III	ν(Cu–S)
I	2900/2825	1260	990	a
II	2920/2860	1280	1000	365
III	2900/2840	1285	1015	355
IV	2925/2845	1280	1020	355
V	2945/2850	1300	1045	355
VI	2925/2850	1255	995	340
VII	2945/2840	1280	995	340
VIII	2920/2850	1290	995	a
IX	2900/2840	1310	1015	345
X	2940/2840	1340	990	a

[a] No associated ν(Cu–S) activity was observed.

Infrared Spectra

Infrared spectra of studied complexes are in agreement with the X-ray diffraction data with respect to the monodentate sulphur donating character. Table 5 lists some selected bands and their assignments of the compounds reported here.

The ν(NH) in the complexes appears as two broad bands at about 2900 and 2840 cm^{-1} and is shifted to lower wave numbers by about 250 cm^{-1}, using as reference the values of 3180–3140 cm^{-1} obtained from the solid state spectra of the free ligands. These observed significant shifts confirm the existence of strongly hydrogen bonded N–H groups [30].

The spectra of the free ligands, apart from various ring vibrations, exhibit the usual thioamide bands [31, 32] in the regions ~1510, 1320, 1000 and 750 cm^{-1} assignable to the thioamide I, II, III and IV respectively, and suggesting that the ligands exist in the thione form in the solid state. In the spectra of the complexes thioamide II and thioamide III show a shift to lower wave numbers (~10–30 and 10–55 cm^{-1} respectively) since the coordination takes place through the sulphur atom. Thioamide I and thioamide IV are partly masked by strong triphenylphosphine absorptions.

The monodentate nature of the ligands is further confirmed by far IR spectra, wherein new bands are observed around 365–340 cm^{-1} which can be assigned to (Cu–S) vibration [31]. This assignment is supported by the absence of absorptions in the region where ν(Cu–N) generally lies.

Ionic nitrate is indicated by the presence of an intense band at ~1380 cm^{-1} (ν_3) as well as a band of medium intensity at ~820 cm^{-1} (ν_2) in the solid state infrared spectra of all complexes [33].

Electronic and NMR Spectra

The UV–Vis spectra of the compounds in CHCl$_3$ solutions, as expected, show only two absorption bands at ~360 and ~270 nm which can be assigned as intraligand transitions.

As mentioned above, the compounds are diamagnetic and give very sharp proton NMR signals. The NMR measurements show the absence of any evidence for the thiol (–SH) proton, and in some complexes, a peak for the NH group appears in the region ~11–14 ppm. All other signals expected for the thione and PPh$_3$ ligands are observed.

Supplementary Material

Lists of observed and calculated structure factors, of anisotropic thermal parameters of the non-H atoms, of positional and anisotropic thermal parameters of the H atoms and of the positional and equivalent thermal parameters of the phenyl-carbon atoms are available from the authors on request.

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